Gibbs free-energy difference between the glass and crystalline phases of a Ni-Zr alloy

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The heats of eutectic melting and devitrification, and the specific heats of the crystalline, glass, and liquid phases have been measured for a $Ni_{24}Zr_{76}$ alloy. The data are used to calculate the Gibbs free-energy difference, ΔG_{AC}, between the real glass and the crystal on an assumption that the liquid-glass transition is second order. The result shows that ΔG_{AC} continuously increases as the temperature decreases in contrast to the ideal glass case where ΔG_{AC} is assumed to be independent of temperature.

The Gibbs free-energy difference, ΔG, between a metastable phase and a stable phase of materials is an important parameter for investigating the phase stability (e.g., the phase boundary determination) and the kinetics of phase transitions (e.g., the nucleation rate of the stable phase). The free-energy difference as a function of temperature, T, can be experimentally determined by the following equation

$$\Delta G(T)=\left(\Delta H_t+\int_T^{T_t}\Delta C_p\,dT\right)-\left(\Delta S_t+\int_T^{T_t}\Delta C_p/T\,dT\right), \quad (1)$$

where ΔH_t and ΔS_t are the enthalpy and entropy differences at the equilibrium transition temperature, T_t, and ΔC_p is the specific heat difference between the metastable and stable phases.

If a glass phase is involved in an application of Eq. (1), there is a problem because the glass transition appears to be a kinetic process and the existence of the equilibrium temperature of the glass with either the liquid or crystalline phases is still an open question. One way to circumvent this problem and obtain an approximate value for ΔG is as follows:[1] The glass is considered as a frozen liquid which is isoentropically transformed from the supercooled liquid at the temperature at which the entropy of the supercooled liquid is equal to that of the corresponding crystal. The glass obtained with this hypothetical procedure is called the "ideal glass" and the transition temperature, T_K, is named after Kauzmann who first pointed out the possibility of such an isoentropic temperature.[2] The entropy (or the specific heat) of the glass below T_K is assumed to be equal to that of the crystal; therefore, the free-energy difference between the glass and the crystal is independent of temperature, and is given by the difference between the supercooled liquid and the crystal at T_K.

The specific heats of highly supercooled liquids are not generally available; therefore, they must be estimated by extrapolating the values at high temperatures. It is known that T_K determined by employing the extrapolated value is lower than the experimental glass transition temperature, T_g, by typically 50 K.[3] This discrepancy is usually attributed to the finite cooling and heating rates of experiments.[4,5] Further, the specific heat of the "real glass," in contrast to the ideal glass, is slightly larger than that of the crystal. It is of interest to investigate the improvement in the approximation if we take into account these experimental facts. In this letter, we present the result of an investigation on Ni-Zr alloys which have been extensively studied partly because the glasses are formed by not only the liquid quenching techniques but also the solid-state amorphization techniques.[6]

We have chosen an eutectic alloy whose composition is $Ni_{24}Zr_{76}$. The eutectic liquid is in equilibrium with the mixture of $NiZr_2$ and βZr phases at 1233 K. Buttons of the alloy were prepared by induction melting of 99.999% pure Ni and 99.9% pure Zr on a silver boat in an Ar atmosphere. The buttons were then cut into small pieces for further processing and measurements. The glass samples were produced by splat quenching under an Ar atmosphere. X-ray diffraction was used to identify the phases in the processed samples. For calorimetric measurements, a Perkin–Elmer DSC 4 and a drop calorimeter were used. We have previously reported a detailed description of the latter[7] and its application to a supercooled liquid.[8]

The specific heat of the stable crystalline phases (a mixture of $NiZr_2$ and αZr), C_p^C, was measured by the DSC with a sapphire standard. The result is shown in Fig. 1 as the solid circles. The DSC could measure C_p^C up to 900 K; however, the data above 515 K were discarded because of the apparent contamination due to oxidation. The best fit of the data through linear regression is

$$C_p^C(T)=24.3+6.59\times10^{-3}T \quad \text{(J/mol K)}. \quad (2)$$

Equation (2) is comparable to $C_p^C(T)=26.3+2.80\times10^{-3}T$ J/mol K, the weighted average of the specific heat data of $NiZr_2$ and αZr as reported by Smith *et al.*[9]

X-ray diffraction showed that the splat-quenched samples whose thickness were less than 40 μm were predomi-

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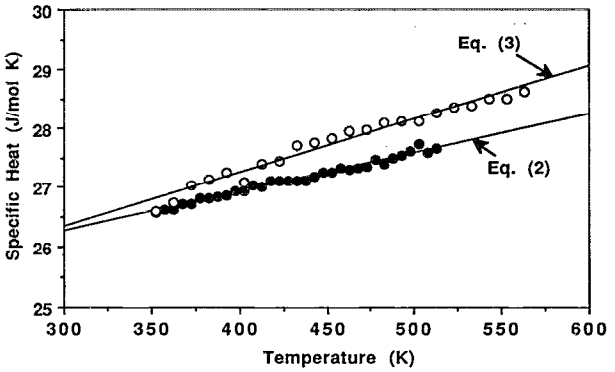

FIG. 1. The specific heats of the glass and crystal of the $Ni_{24}Zr_{76}$ alloy. Equations (2) and (3) are the linearly fitted equations.

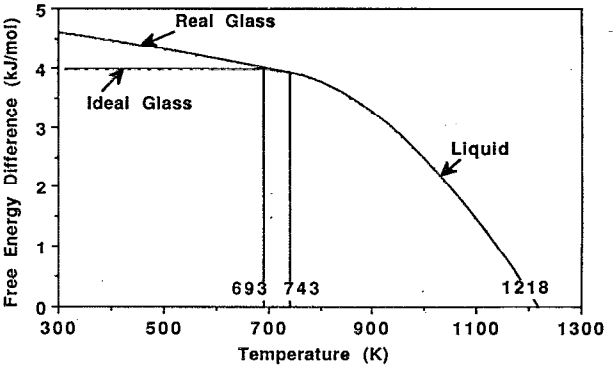

FIG. 3. The Gibbs free-energy difference between the glass and the crystal for the $Ni_{24}Zr_{76}$ alloy.

nately the glass phase. The glass sample was heated up in the DSC at 20 K/min and devitrification was observed. As a result, T_g cannot be directly determined. The devitrification temperature T_d and the heat of devitrification ΔH_d were determined to be 613 K and 5.4 kJ/mol, respectively, with a Pb standard sample. X-ray diffraction showed that the devitrified sample was the mixture of the stable phases. The ΔH_d value is in good agreement with that of Altounian *et al.*[10] but smaller than that of Henaff *et al.*[11] The specific heat of the glass, C_p^A, is measured from 350 to 565 K. The result is shown in Fig. 1 as the open circles. The best fit of the data through regression is

$$C_p^A(T)=23.7+8.79\times10^{-3}T \quad \text{(J/mol K)}. \tag{3}$$

Numerically, Eq. (3) is slightly larger than Eq. (2), which is consistent with the cases of the other metallic glasses.

The enthalpy of the liquid alloy, $H^L(T)$, above and below the melting point was measured by the drop calorimeter. X-ray diffraction showed that the processed samples were the mixture of the stable phases. The result is shown in Fig. 2 as the solid circles. The maximum supercooling level is approximately 120 K for the present case. For the presentation, the enthalpy of the crystalline phase mixture at 298 K is assigned to zero. The data is fitted by linear regression. The result is

$$H^L(T)=-22.4+5.42\times10^{-2}T \quad \text{(kJ/mol)}. \tag{4}$$

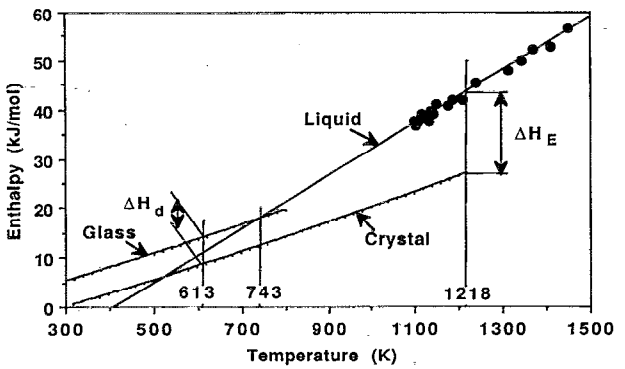

FIG. 2. The enthalpies of the liquid, glass, and crystal of the $Ni_{24}Zr_{76}$ alloy.

By definition, the specific heat of the liquid, C_p^L, is given by

$$C_p^L=dH^L(T)/dT=54.2 \quad \text{(J/mol K)}. \tag{5}$$

The $H^L(T)$ curve is extrapolated on an assumption that C_p^L remains constant down to room temperature, although the specific heats of glass-forming liquids are known to increase as the supercooling level increases.[12]

The enthalpy curves of the crystalline phase mixture, H^C, and the glass, H^A, are also shown in Fig. 2. These curves are obtained in the following manner: The H^C curve is calculated by integrating Eq. (2) from 298 K to the eutectic temperature, T_E, of the $NiZr_2$-αZr pseudobinary alloy. We calculated T_E and the eutectic composition by employing a simple solution model. The results are 1218 K and $Ni_{23}Zr_{77}$, respectively. Since the shift of the eutectic composition is very small, the present alloy is considered to be the eutectic alloy. The enthalpy change associated with the eutectic melting, ΔH_E, is determined to be 16.4 kJ/mol. It is now possible to obtain T_K by calculating the entropy curves of the liquid and crystalline phases using C_p^L, C_p^C, and ΔH_E. The result is that T_K is approximately 693 K. In order to place the H^A curve with respect to either the H^C or H^L curves in Fig. 2, we take a reference point at T_d by adding ΔH_d to $H^C(T_d)$ as shown in the figure. Once the reference point is assigned, the H^A curve can be calculated by integrating Eq. (3) from T_d to T. In Fig. 2, the H^A curve is extrapolated above T_d on an assumption that Eq. (3) remains valid. The H^A curve intersects the H^L curve at T_g, which is calculated to be 743 K.

Since the glass transition is assumed to be second order, the entropy of the liquid is also equal to that of the glass at T_g. The free-energy difference between the real glass and the crystalline phases, ΔG_{AC}, can now be calculated by applying Eq. (1) to the supercooled liquid and the crystal from T_E to T_g, and then to the glass and the crystal below T_g. The result is shown in Fig. 3. For comparison, the free-energy difference of the ideal glass, ΔG_{AC}^{id}, is also shown in the figure. Contrary to ΔG_{AC}^{id} which remains constant, ΔG_{AC} increases approximately linearly as the temperature decreases. This increase occurs because of the excess entropy which exists in the real glass as opposed to the ideal glass whose entropy is assumed to be equal to that of the crystal.

We have demonstrated a procedure to determine the Gibbs free-energy difference between the real glass and the corresponding crystal based on the experimental data. The procedure assumes that the specific heats of the supercooled liquid and the glass can be smoothly extrapolated and the glass transition is second order. The former assumption is generally accepted except near T_g where the atomic relaxation time is comparable to the experimental time scale. The latter may be supported by the fact that the enthalpy change associated with the glass transition appears to be zero and the specific heat discontinuously changes at T_g. These are indicative of the second-order transition.

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